

PATENT SPECIFICATION

(11) 1 405 308

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 368 36Y 456 45Y 574 620 623 624 62X 62Y 630
 633 63Y 64Y 652 656 660 662 670 676 680 699
 KH KJ LY NB
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(72) Inventors GUNTHER LAMM and JOHANNES DEHNERT

(54) AMINO-PYRIDINES AS COUPLING COMPONENTS FOR AZO DYES

(71) We, B.A.S.F. AKTIENGESSELLSCHAFT a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, formerly Badische Anilin- & Soda-Fabrik Aktiengesellschaft, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to amino-pyridines of the formula



(I)

in which

X is CN or CONH₂;

R¹ is H, C₂ to C, alkyl or phenyl;

one Q is NHR; and the other is Cl, NH₂ or NHR;

where R denotes or each R independently denotes a substituted or unsubstituted hydrocarbon radical;

and also to amino-pyridines of the same formula, in which R¹ is methyl;

X and one Q can denote any of the values specified above for X and Q respectively, and the other Q is NHR⁴;

where R⁴ is

a) an alkyl group of more than 8 carbon atoms;

b) a 5-hydroxy-1,5-dimethyl-hexyl group;

c) an optionally hydroxy-substituted aralkyl group with 3 or 4 carbon atoms in the alkyl chain;

d) a $(CH_2)_m$ — group where m is from 4 to 6;

e) a cyanoalkyl group; or

f) a hydrocarbon or substituted hydrocarbon group which,

(i) is or contains a cycloalkyl, polycycloalkyl, cycloalkenyl or polycycloalkenyl group containing 5 or from 7 to 12 carbon atoms

(ii) is or contains a cycloalkyl or polycycloalkyl group which bears chloro, alkyl, hydroxyalkyl, chloroalkyl or hydroxyethoxy as a substituent;

(iii) contains as a substituent an aralkoxy or cycloalkyloxy group;

(iv) contains at least two OC₂H₅ groups and in all at least 3 ether oxygen atoms; or

(v) is a derivative (other than an acyl derivative) of, or contains as a substituent a methyl-substituted oxyethylene group. These amino pyridines are intermediates for azo dyes. The phrase "contains as a substituent" as applied

[Price 33p]

to a substituted or unsubstituted hydrocarbon group includes the case where the substituent is a secondary substituent: e.g. class f(iii) above includes the radical $(\text{CH}_2)_3\text{OC}_2\text{H}_4\text{O-cyclohexyl}$.

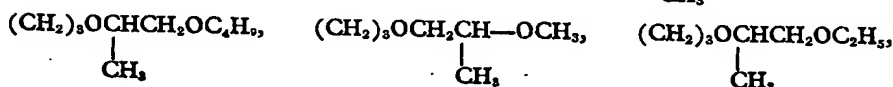
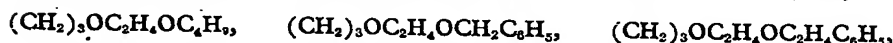
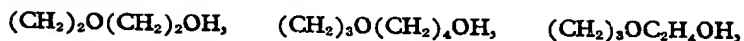
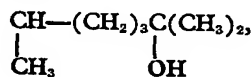
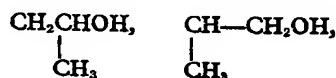
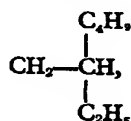
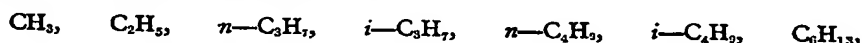
The invention also relates to mixtures in any proportion of compounds as specified with the isomeric compounds in which the two Q's are interchanged.

Examples of alkyl radicals R^1 are ethyl, n-propyl, isopropyl, butyl, pentyl, α -ethylpentyl and preferably methyl.

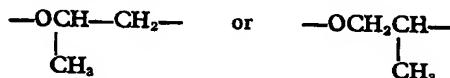
Examples of radicals R are alkyl of one to eight carbon atoms which may be interrupted by oxygen atoms and which may bear hydroxy, alkoxy, cyano, cycloalkoxy, aralkoxy or aroxy as substituents, cycloalkyl and polycycloalkyl which may bear hydroxy, chloro, hydroxyalkyl, chloroalkyl or alkyl as substituents, aralkyl of seven to fifteen carbon atoms, phenyl which may bear chloro, hydroxy, alkoxy, alkyl, hydroxyalkoxy or hydroxyalkyl as substituents, or alkenyl, pyrrolidonylalkyl or carboxyalkyl.

Examples of individual radicals R are:

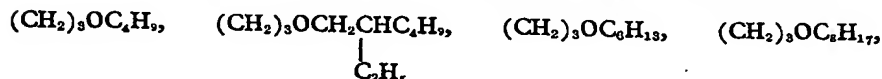
(1) unsubstituted or substituted alkyl:

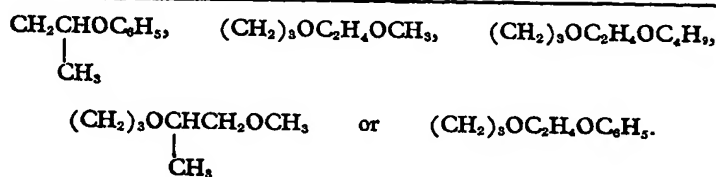


corresponding radicals in which the groupings $\text{---OC}_2\text{H}_4\text{---}$,

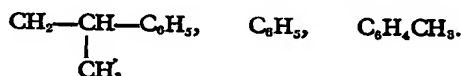
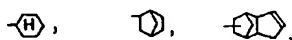


are present twice, three times or four times,





Examples of preferred oxygen-free radicals R are:

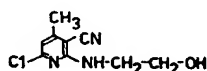


The new coupling components are outstandingly suitable for the production of azo dyes by reaction with diazotized amines. The dyes which can be obtained in this way are distinguished by excellent fastness properties and by an unusual brilliance for azo dyes.

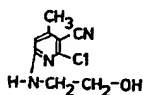
The following Examples illustrate the invention, Examples 2, 33, 35, 36, 43, 46 and 57 to 183 relating to the preparation of compounds according to the invention, and Examples 1, 3 to 32, 34, 37 to 42, 44, 45 and 47 to 56 relating to the preparation of intermediates, which, by reaction with an amine of the formula R^4NH_2 will yield compounds according to the invention. Parts and percentages referred to are by weight unless otherwise stated, and parts by volume stand in the same relationship to parts by weight as does the ml to the g.

Example 1.

187 parts of 2,6-dichloro-3-cyano-4-methylpyridine is suspended in 500 parts by volume of methanol. 80 parts of 2-hydroxyethylamine is then added at 40° to 45°C followed by 100 parts of triethylamine. The mixture is stirred for five to six hours at 45° to 50°C , about 250 parts by volume of methanol is distilled off and the residue is diluted with 1000 parts by volume of water. After acidification with 50 parts of concentrated hydrochloric acid, the whole is stirred for one hour, the deposited precipitate is filtered off, washed with water until neutral and dried. About 210 parts of a colourless powder of the formula:



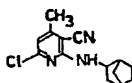
is obtained. The powder contains a smaller amount of a product of the formula:



The mixture melts at 115° to 120°C .

Example 2.

A suspension of 50 parts by volume of methanol, 22 parts of norbornylamine, 37 parts of 2,6-dichloro-3-cyano-4-methylpyridine and 25 parts of triethylamine is stirred for six hours at 40° to 50°C . Then about 200 parts by volume of ice-water is added, the whole acidified to pH 1, the precipitated product of the formula

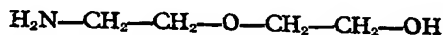


(which still contains a small proportion of 2-chloro-3-cyano-4-methyl-6-norbornyl-aminopyridine isomers) is filtered off, washed with water and dried. About 45 parts of a colourless powder is obtained which melts at 110° to 112°C.

45 parts of the moist powder is heated at 130° to 140°C with 50 parts of the amine

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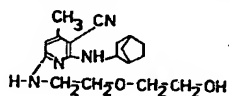
of the formula:



5

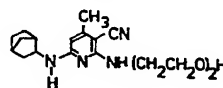
the water being allowed to evaporate. After stirring for five hours at 130° to 140°C the reaction is completed. The whole is allowed to cool and is acidified with 130 parts by volume of acetic acid. A solution of the coupling component mixture of the formulae:

10



(A)

and



(B)

10

the amount of the product of the formula (B) being small.

When the mixture thus obtained is coupled with *p*-nitroaniline a dye is obtained which dissolves in dimethylformamide to give an orange solution.

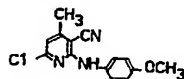
Example 3:

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A mixture of 300 parts by volume of *N*-methylpyrrolidone, 150 parts of 2,6-dichloro-3-cyano-4-methylpyridine, 115 parts of *p*-anisidine and 90 parts of triethylamine is stirred for from six to seven hours at 70°C. It is then poured while stirring onto 1500 parts of ice-water and acidified with hydrochloric acid to pH 1. About 220 parts of a colourless product of the formula:

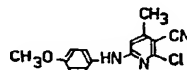
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20

is obtained which is isolated by filtration, washing with water and drying. The powder contains a minor amount of a product of the formula:



The mixture melts at 147° to 150°C.

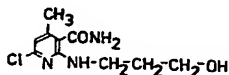
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Example 4.

50 parts of 2,6-dichloro-3-carbamoyl-4-methylpyridine is stirred with 75 parts of propanolamine-1,3 for ten hours at 90°C. The mixture is precipitated with water and acidified to pH < 0. The insoluble residue is filtered off, washed with water and dried. The colourless powder melts at 210°C and probably has the formula (C):

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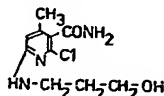
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(C)

30

The filtrate has caustic soda solution added to it until the pH is from 5 to 6. A crystalline precipitate is thrown down which probably has the formula (D)



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This is filtered off, washed with water and dried. The product (D) thus obtained also contains traces of the product of the formula (C) and melts at 150° to 160°C.

35

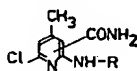
If the reaction mixture is precipitated at pH from 6 to 7, a mixture of the two isomers is obtained which has a melting point of about 143°C.

When 2,6-dichloro-3-carbamoyl-4-methylpyridine is treated with other amines

analogously to the method described in Example 4, mixtures of substituted 2-aminopyridines and 6-aminopyridines are obtained, the amount of 2-amino-3-carbamoyl-4-methyl-6-chloropyridine derivatives being only slightly greater than that of the 6-aminopyridine isomers in question.

5 The physical properties given in Table 1 (which lists some compounds which may be prepared as mentioned above) relate to mixtures of the compounds indicated with their isomers in which Cl and NHR are interchanged. 5

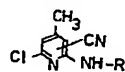
TABLE 1



No.	R	Melting point °C
5		115 - 199
6	$-(CH_2)_3O-C_2H_5$	120
7	$-C_4H_9(n)$	121 - 122
8	$-C_6H_{13}(n)$	89 - 90
9	$-CH_2CH-CH_3$ OH	140 - 145
10		180 - 190
11	$(CH_2)_3OCH_3$	105
12	$C_3H_7(n)$	124
13	CH_2CH_2OH	130
14	$(CH_2CH_2O)_2H$	110
15	CH_3	>150
16	C_2H_5	143
17		190

10 When 2,6-dichloro-3-cyano-4-methylpyridine is treated with other amines by a method analogous to those described in Examples 1 to 3, there are obtained (by exchange of one chlorine atom) mixtures of 2-amino-6-chloro- and 2-chloro-6-amino-3-cyano-4-methylpyridine derivatives, the proportion of the 2-chloro-3-cyano-4-methyl-6-amino isomers as a rule being noticeably less. The physical properties given in Table 2 (which lists some compounds which may be prepared as mentioned above) relate to mixtures of the compounds indicated with their isomers in which Cl and NHR are interchanged. 15

TABLE 2



No.	R	Melting point °C
18	$(\text{CH}_2)_5 \text{COONa}$	85 – 91
19	$(\text{CH}_2)_5 - \text{CH}_3$	40 – 47
20	$(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	79 – 83
21	$(\text{CH}_2)_2\text{OCH}_3$	90 – 100
22	$\text{C}_4\text{H}_9(\text{n})$	50 – 60
23	$\text{C}_3\text{H}_7(\text{i})$	95 – 105
24	$(\text{CH}_2)_3\text{OCH}_3$	75 – 85
25	$\begin{array}{c} \text{CH}_2\text{CH}-\text{C}_4\text{H}_9(\text{n}) \\ \\ \text{C}_2\text{H}_5 \end{array}$	greasy product
26	$(\text{CH}_2)_3\text{OH}$	110 – 114
27	$(\text{CH}_2)_2\text{OH}$	125
28		145 – 154
29		147 – 149
30	H	225 – 230
31		165 – 175
32		103 – 105
33	$\begin{array}{cc} \text{CH}(\text{CH}_2)_3\text{C}(\text{CH}_3)_2 \\ \quad \quad \\ \text{CH} \quad \quad \text{OH} \end{array}$	tar

TABLE 2 cont.













No.	R	Melting point °C.
34		103
35		90 - 92
36	$-(CH_2)_3O-CH_2C_6H_5$	tar becoming solid on prolonged standing
37		105 - 110°
38		170 - 185°
39		147°
40		120 - 128°
41		170°
42	$-(CH_2)-\underset{\substack{ \\ OH}}{CH}-C_6H_5$	115°
43	$-(CH_2CH_2)-\underset{\substack{ \\ CH_3}}{CH}-C_6H_5$	viscous oil
44		185°

TABLE 2 cont.

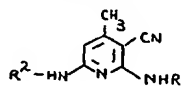
No.	R	Melting point °C.
45	$\text{CH}_2\text{CH}_2\text{COOH}$	170°
46	$-\text{C}_{14}\text{H}_{29}$	62°
47		130 – 140°
48		160°
49	$-\text{CH}_3$	140°
50	$\begin{array}{c} -\text{CH}_2-\text{CH}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	80°
51	$(\text{CH}_2)_3\text{O}-(\text{CH}_2)_2\text{OH}$	75 – 80°
52	$(\text{CH}_2)_3\text{O}-\text{C}_8\text{H}_7(\text{i})$	oil
53	$\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_5$	118 – 123°
54	$(\text{CH}_2)_3\text{O}-\text{C}_2\text{H}_4\text{O}-\text{C}_6\text{H}_5$	oil
55		172°
56		oil

When the products set out in Tables 1 and 2 are treated with aliphatic or aromatic amines at temperatures above 100° or 80°C respectively, the corresponding coupling products of formula (I) are obtained.

In the case of pyridine derivatives which contain a carbamoyl group the reaction has to be carried out however at the lowest possible temperature because otherwise hydrolysis and/or decarboxylation of the $-\text{CONH}_2$ group may take place.

The following tables illustrate the products which may be obtained by methods hereinbefore described. Where the 2-substituent and the 6-substituent in the product are not the same the physical properties in each case relate to a mixture of the compound indicated with its isomer in which the 2- and 6-substituents are interchanged.

TABLE 3



No.	R	R ²	Physical Properties
57	H	$(\text{CH}_2)_3\text{-O-CH}_2\text{-C}_6\text{H}_5$	viscous oil
58	H	$(\text{CH}_2)_3\text{-O-CH}_2\text{CH}_2\text{-C}_6\text{H}_5$	"
59	H	$(\text{CH}_2)_3\text{-O-CH(CH}_3\text{)-OCH}_3$	"
60	H	$\text{-CH(CH}_3\text{)-C(CH}_3\text{)}_2\text{OH}$	"
61	H	$(\text{CH}_2)_3\text{O(CH}_2\text{CH}_2\text{O)}_2\text{CH}_3$	"
62	H	$(\text{CH}_2)_3\text{O(CHCH}_2\text{O)}_2\text{CH}_3$	"
63		H	"
	R	R ²	Shade on coupling with
64	$(\text{CH}_2)_3\text{OCH}_2\text{C}_6\text{H}_5$	$\text{-CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	orange
65	"	$(\text{CH}_2)_3\text{OH}$	"
66	"	$\text{CH}_2\text{CH}_2\text{OH}$	"
67	$\text{CH}_2\text{CHOC}_6\text{H}_5$	"	"
68	"	$(\text{CH}_2)_3\text{OH}$	"
69	$(\text{CH}_2)_3\text{O-CH}_2\text{CH}_2\text{C}_6\text{H}_5$	$\text{-CH}_2\text{CH}_2\text{OH}$	"
70	"	$(\text{CH}_2)_3\text{OH}$	"
71	$\text{CH}_2\text{-}\langle\text{H}\rangle\text{-CH}_2\text{OH}$	$\text{-CH}_2\text{CH}_2\text{OH}$	"

TABLE 3 cont.

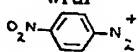
No.	R	R ²	Shade on coupling with
			
72	$\text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2\text{OH}$	$-(\text{CH}_2)_3\text{OH}$	orange
73	"	$(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	"
74	$-(\text{CH}_2)_3\text{OCHCH}_2\text{O}-\text{C}_6\text{H}_5$ CH_3	$-\text{CH}_2\text{CH}_2\text{OH}$	"
75	"	$-(\text{CH}_2)_3\text{OH}$	"
76	CH_3 $-\text{CH}(\text{CH}_2)_2-\text{C}_6\text{H}_4-\text{OH}$	$-\text{CH}_2\text{CH}_2\text{OH}$	"
77	"	$-(\text{CH}_2)_3\text{OH}$	"
78	"	$-(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	"
No.	R	R ²	Physical Properties
79	$(\text{CH}_2)_3\text{O}-\text{CHCH}_2\text{OCH}_3$ CH_3	$-\text{CH}_2-\text{CH}-\text{C}_6\text{H}_5$ OH	viscous oil
80	$-\text{CH}(\text{CH}_2)_3\text{C}(\text{CH}_3)_2$ CH_3 OH	$-\text{CH}(\text{CH}_2)_3\text{C}-(\text{CH}_3)_2$ CH_3 OH	"
81	"	$-\text{CH}_2\text{CH}_2\text{OH}$	"
82	"	$-(\text{CH}_2)_3\text{OH}$	"
83	"	$-\text{CH}_2\text{CHOH}$ CH_3	"
84	"	$-(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	"
85	"	$-(\text{CH}_2)_3\text{O}-(\text{CH}_2)_2\text{OH}$	"
86	"	$-(\text{CH}_2)_3\text{O}(\text{CH}_2)_4\text{OH}$	"
87	"	$-(\text{CH}_2)_3\text{O}(\text{CH}_2)_6\text{OH}$	"
88	"	$-(\text{CH}_2)_2\text{OCH}_3$	"
89	"	$-(\text{CH}_2)_3\text{OCH}_3$	"
90	"	$-(\text{CH}_2)_3-\text{O}-\text{C}_3\text{H}_7$	"
91	$-(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	$-\text{CH}(\text{CH}_2)_3-\text{C}(\text{CH}_3)_2$ CH_3 OH	"

TABLE 3 cont.




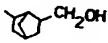
No.	R	R ²	Physical properties
92	$-(CH_2)_2OH$	$\begin{array}{c} -CH(CH_2)_3-C(CH_3)_2 \\ \quad \quad \\ CH_3 \quad \quad OH \end{array}$	viscous oil
93	$-(CH_2)_3OH$	"	"
94	$\begin{array}{c} -CHCH_2OH \\ \\ CH_3 \end{array}$	"	"
95	$\begin{array}{c} -CHCH_2OH \\ \\ C_3H_7 \end{array}$	"	"
			Shade on coupling with
			
No.	R	R ²	Physical Properties
96	$-CH_2CH_2OCH_2CH_2OH$		orange
97	"	$-(CH_2)_3-O-\langle H \rangle$	"
98	$(CH_2)_3-O-(CH_2)_2OH$		viscous oil
99	"		"
100	"	$(CH_2)_3-O-\langle H \rangle$	"
101	$(CH_2)_3-O-\langle H \rangle$	$-CH_2CH_2OH$	"
102	"	$-(CH_2)_3OH$	"
103	"	$(CH_2)_2O(CH_2)_2OH$	"

TABLE 3 cont.



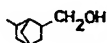

No.	R	R ²	Physical Properties
104	$\text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2\text{OH}$	$(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$	viscous oil
105	"	$(\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{OH}$	"
106	$\text{C}_6\text{H}_4 - \text{OCH}_2\text{CH}_2\text{OH}$	$-\text{CH}_2\text{CH}_2\text{OH}$	"
107	"	$-(\text{CH}_2)_3\text{OH}$	"
108	"	$-(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$	"
109		"	"
110	"	$-(\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{OH}$	"
111		"	"
112		"	"
113	"	$-(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$	"
114		"	"
115	$-\text{CH}(\text{CH}_3)(\text{CH}_2)_2 - \text{C}_6\text{H}_4 - \text{CH}_3$	$-\text{CH}_2\text{CH}_2\text{OH}$	"

TABLE 3 cont.






No.	R	R ²	Shade on coupling with 
116		-C ₂ H ₅	orange
117	"	-C ₃ H ₇	"
118		-C ₄ H ₉	"
119	"	-CH ₂ CH ₂ OH	"
120	"	-(CH ₂) ₃ OH	"
121	"	-(CH ₂) ₂ O(CH ₂) ₃ OH	"
122	"	-(CH ₂) ₂ OCH ₃	"
123	"	(CH ₂) ₃ O(CH ₂) ₂ OH	"
124	"	(CH ₂) ₃ O(CH ₂) ₄ OH	"
125		C ₂ H ₅	"
126	"	C ₃ H ₇ (n)	"
127	"	C ₄ H ₉ (n)	"
128	"	C ₆ H ₁₃ (n)	"
129	H		reddish yellow

TABLE 3 cont.



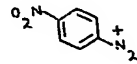

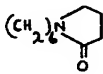
No.	R	R ²	Shade on coupling with 
130		-CH ₂ CH ₂ OH	orange
131	"	(CH ₂) ₅ OH	"
132	"	(CH ₂) ₂ O(CH ₂) ₂ OH	"
133	"	(CH ₂) ₃ O(CH ₂) ₂ OH	"
134	"	(CH ₂) ₃ O(CH ₂) ₄ OH	"
135	"	(CH ₂) ₂ OCH ₃	"
136	"	(CH ₂) ₃ OCH ₃	"

TABLE 4

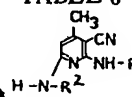
$ \begin{array}{c} \text{R}^1 \\ \text{CN} \\ \text{R}^2\text{-HN} \quad \text{N} \quad \text{NH-R} \end{array} $				Shade on coupling with
No.	R	R ²	R ¹	$ \text{O}_2\text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{N}_2^+ $
137	CH ₂ CH ₂ C ₆ H ₅	CH ₂ CH ₂ OH	H	orange
138	"	"	-C ₂ H ₅	"
139	"	(CH ₂) ₃ OH	"	"
140	"	(CH ₂) ₂ O(CH ₂) ₂ OH	H	"
141	"	"	C ₂ H ₅	"
142	"	CH ₂ CH ₂ OH	C ₃ H ₇ (n)	"
143	$ \begin{array}{c} \text{CH}_2\text{CH}-\text{C}_6\text{H}_5 \\ \\ \text{OH} \end{array} $	"	H	"
144	"	"	C ₃ H ₇ (n)	"
145	"	(CH ₂) ₃ OH	"	"
146	"	"	H	"
147	"	"	C ₂ H ₅	"
148	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	$ \begin{array}{c} -\text{CHC}_4\text{H}_9(n) \\ \\ \text{C}_2\text{H}_5 \end{array} $	"
149	"	"	-C ₈ H ₁₇ (n)	"
150	CH ₂ CH ₂ OCH ₃	(CH ₂ CH ₂ O) ₂ H	-C ₆ H ₅	"
151	(CH ₂) ₃ OCH ₃	"	"	"
152	H	$ \begin{array}{c} \text{CH}_2\text{CH}-\text{C}_6\text{H}_5 \\ \\ \text{OH} \end{array} $	H	reddish yellow
153	H	"	-C ₃ H ₇ (n)	"
154	H	(CH ₂) ₃ O(CH ₂) ₄ OH	H	"
155	H	(CH ₂) ₃ O(CH ₂) ₂ OH	H	"

TABLE 5

No.	R	R ²	Shade after coupling with
			
156	$-(CH_2)_3O-CH_2C_6H_5$	$-(CH_2)_2OH$	red
157	„	$-(CH_2)_3OH$	„
158	$\begin{array}{c} -CH(CH_2)_3C(CH_3)_2 \\ \quad \\ CH_3 \quad OH \end{array}$	$-CH_2CH_2OH$	„
159	„	$-(CH_2)_3OH$	„
160	„	$-(CH_2)_2O(CH_2)_2OH$	„
161		$-(CH_2)_2O(CH_2)_2OH$	„
162		„	„
163	$-(CH_2)_3-O-\langle H \rangle$	$-(CH_2)_2O-(CH_2)_2OH$	„
164	„	$-(CH_2)_2OH$	„
165	$-(CH_2)_3-O-\langle H \rangle$	$-(CH_2)_3OH$	„
166	$\begin{array}{c} -CH_2-CH-C_6H_5 \\ \\ CH_3 \end{array}$	„	„
167	„	$-(CH_2)_2OH$	„
168	„	$-(CH_2)_2O(CH_2)_2OH$	„
169	$\begin{array}{c} -CH_2-CH-O-C_6H_5 \\ \\ CH_3 \end{array}$	$-CH_2-CH_2-OH$	„

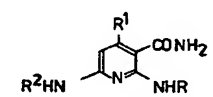
The Examples described in Tables 3, 4 and 5 are prepared by always first introducing the radical R.

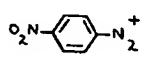

TABLE 6



No.	R	R ²	Melting point °C.
170	$-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{C}_6\text{H}_5$	$-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{C}_6\text{H}_5$	ca. 60
171	$-\text{C}_{14}\text{H}_{29}$	$-\text{H}$	ca. 90 - 105
172	$-\text{H}$	$-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{C}_6\text{H}_5$	tar
173	$-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{C}_6\text{H}_5$	$-\text{H}$	tar
174	$-\text{CH}_2-\text{CH}_2-\text{CN}$	$-\text{CH}_2-\text{CH}_2-\text{CN}$	170-176
175	$-\text{CH}_2-\text{CH}_2-\text{CN}$	$-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_5$	ca. 120
176	$-\text{H}$	$-(\text{CH}_2)_5\text{CN}$	142

TABLE 7



Example	R ¹	R	R ²	Shade when coupled with 
177	C_3H_7	C_6H_5	$\text{CH}_2\text{CH}_2\text{OH}$	bluish red
178	"	"	$(\text{CH}_2)_3\text{OH}$	"
179	"	"	$(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$	"
180	"		$(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$	"
181	"	"	$\text{CH}_2\text{CH}_2\text{OH}$	"
182	"	"	$(\text{CH}_2)_3\text{OH}$	"
183	H	C_6H_5	$(\text{CH}_2)_3\text{OH}$	"

WHAT WE CLAIM IS:—

1. An amino-pyridine of the formula



in which

R¹ is H, C₁ to C₇ alkyl or phenyl;X is CN or CONH₂; andone Q is NHR; and the other is Cl, NH₂ or NHR; where

R denotes, or each R independently denotes, a substituted or unsubstituted hydrocarbon radical.

2. An amino-pyridine of the formula




in which

R¹ is methyl;X and one Q can denote any value specified in claim 1 for X and Q respectively; and the other Q is NHR⁴;where R⁴ is

a) an alkyl group of more than 8 carbon atoms;

b) a 5-hydroxyl-1,5-dimethyl-hexyl group;

c) an optionally hydroxy-substituted aralkyl group with 3 or 4 carbon atoms in the alkyl chain;

d) a $(CH_2)_m$ — group where m is from 4 to 6;

e) a cyanoalkyl group; or

f) a hydrocarbon or substituted hydrocarbon group which,

(i) is or contains a cycloalkyl, polycycloalkyl, cycloalkenyl or polycycloalkenyl group containing 5 or from 7 to 12 carbon atoms,

(ii) is or contains a cycloalkyl or polycycloalkyl group which bears chloro, alkyl, hydroxyalkyl, chloroalkyl or hydroxyethoxy as a substituent;

(iii) contains as a substituent aralkoxy or cycloalkyloxy group;

(iv) contains at least two OC₂H₅ groups and in all at least 3 ether oxygen atoms; or

(v) is a derivative (other than an acyl derivative) of, or contains as a substituent a methyl-substituted oxyethylene group.

3. An amino-pyridine as claimed in claim 1 or 2 in which both Q's are amino groups.

4. An amino-pyridine as claimed in any preceding claim, in which each Q independently is as hereinbefore specifically exemplified.

5. An amino-pyridine as claimed in claim 1, 2, 3 or 4 and as disclosed in any of the foregoing Examples 2, 33, 35, 36, 43, 46 or 57 to 183.

6. A process for preparing an amino-pyridine as claimed in claim 1 or 2 wherein NH₃ or one or more primary amines are reacted with a chloro-pyridine of the formulawhere one Q is chlorine and the other has any of the values specified for Q in the said claim, and X and R¹ are as specified in the said claim.

7. A process as claimed in claim 6 wherein a dichloro pyridine of the formula specified therein, is reacted in two stages to form a diamino-pyridine.

8. A process as claimed in claim 6 or 7 wherein the reaction or one stage of the reaction is carried out substantially as described in any of the foregoing Examples.

9. An amino-pyridine when prepared by a process claimed in claim 6, 7 or 8.

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Agents for the Applicants.

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